Molecular mechanics and equation of state modeling of compressible polyolefin solutions: Impact of pressure and cut-off radius of intermolecular potentials
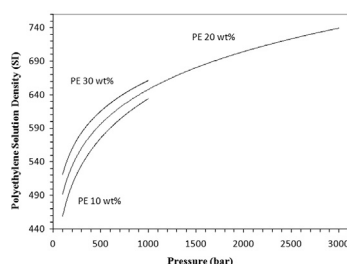
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HIGHLIGHTS

- The MD-simulated densities compare quite favorably with experimental and EOS data.
- A minimum cut-off is suggested for intermolecular forces to obtain accurate properties.
- Depending on the pressure regime an effective cut-off is calculated.
- Pressure has significant impact on structural properties of PE solution.
- As P raises first peak in RDF increases and curve shifts to shorter separations.

GRAPHICAL ABSTRACT

ABSTRACT

This paper reports on the density of solutions of polyethylene (PE) in hexane using molecular dynamics (MD) simulations based upon the accurate OPLS-AA force field at high pressures and 425 K. The NPT–MD simulations are carried out at polymer concentration of 20 wt% in hexane in the pressure range from 100 to 3000 bar. For PE solutions of 10 and 20 wt% the pressure is varied from 100 to 1000 bar. Additionally, the PE solution densities are calculated based on the modified Sanchez–Lacombe (MSL) equation of state (EOS) model to examine the accuracy of the MD computations. The simulated densities increase monotonically with increasing external pressure and compare quite favorably with the experimental and EOS data. It is also revealed that the MSL EOS model produces identical mixture densities regardless of the type of the b parameter. The effect of cut-off radius to density is investigated and it is shown that the solution density increases as cut-off radius increases. A minimum cut-off radius of 1.1 nm is suggested for the intermolecular forces for accurate densities at pressures below 100 bar. For higher pressures density and non-bonded interactions display less sensitivity to cut-off distance. Analysis of the pair distribution function versus pressure is carried out where the height of the first peak increases and the radial distribution function shifts to shorter separations reflecting structural change of the condensed phase. The molecular modeling approach employed in this research provides a good insight into the polymer–polymer, polymer–solvent, and solvent–solvent interactions. The implemented methodology using the OPLS-AA force field and constant pressure/temperature algorithms compare well with the literature data, suggesting the validity of the proposed method.

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1. Introduction

Polyethylene (PE), one of the most widely used plastic materials occupying a crucial position in the polyolefin market, is widely

produced by the solution polymerization process. In solution polymerization, ethylene reacts under high pressures to produce PE while dissolved in an inert hydrocarbon solvent mixture (typically pentane to octane). Hexane and cyclohexane are commonly used as the main components of the inert hydrocarbon solution. In the production of linear low-density polyethylene (LLDPE) co-monomers are added during the polymerization to control the branching in the molecule. In subsequent processing steps, the solution undergoes a series of separations by depressurizing the reactor effluent to purify the PE product and recover the unreacted ethylene and the solvent for recycling. The pressure decrease also affects the density of the mixture, which consequently influences the phase equilibria and process design. As a result, a full characterization of the thermodynamic and physical properties of polymer solution including changes in pressure and mixture density is of great interest from a fundamental scientific point of view and also due to its importance in a wide variety of technological applications (Ghiass and Rey, 2008, 2009a, 2009b; Rasouli and Rey, 2011). Although elevated pressures are involved in the solution polymerization process of PE, few experimental studies of the pressure dependence of thermodynamic properties such as density have been reported due to the difficulty of carrying out experiments at high pressures and temperatures.

Accordingly, within the last half century, numerous thermodynamic models have been proposed to predict phase equilibria of polymer solutions. Most of these models are revised forms of Flory–Huggins lattice theory where density is assumed constant. These models, therefore, cannot predict phase behavior of compressible systems especially where pressure and temperature changes are significant. Recently, to investigate the equilibrium thermodynamics of compressible polymer solutions, the well-known Sanchez–Lacombe (SL) equation of state (EOS) (Sanchez and Lacombe, 1976, 1978; Lacombe and Sanchez, 1976) and its modified version known as the modified Sanchez–Lacombe (MSL) EOS (Koak and Heidemann, 1996) have been extensively used. The SL EOS is a statistical mechanical model that is capable of describing phase behavior of polymer solutions. The speed and accuracy of the MSL equation make it a powerful tool for modeling the polyolefin solutions. To apply the MSL equation for binary mixtures requires an accurate parameterization to obtain the pure component parameters and binary interaction parameters, determined by fitting of the experimental values with theoretical ones. The MSL parameters for the solvent are typically calculated using the parameterization based on molar masses, critical temperatures, critical pressures, and acentric factors. In case of PE, parameters may be obtained by manipulating the PE lattice energy to fit the liquid–liquid critical point and cloud point boundaries of different PE+hydrocarbon mixtures. The remaining parameters are found by minimizing the errors in the liquid density data of pure PE for the specified lattice energy (Krenz et al., 2009). Hence, although there is an abundance of well-established thermodynamic models to describe phase behavior of polymer solutions, in many cases difficulties arise mainly due to the lack of experimental data for the determination of model parameters. Moreover, the problem becomes complex in case of multicomponent mixtures, consistent with industrial polymer production. Thus, alternative methods are undoubtedly required to capture pressure dependence of physical properties of polyolefin solution systems without the need for costly and time-consuming experimental efforts.

Lately, the development of molecular modeling techniques has opened a new highway to a more detailed picture on the molecular-level information. Molecular modeling is a rapidly evolving discipline which has unquestionably benefited a lot from advances in computing. Mathematical models such as molecular mechanics and intensive ab initio electronic structure calculations may be applied to chemical problems, but each has practical limitations. For instance, since ab initio models are not parameterized they do not require experimental data for model development, but use of ab initio electronic structure procedures is computationally expensive and the model is restricted to small systems. In contrast to ab initio models, molecular mechanical models need to be parameterized but they enable us to handle large systems. Since the advent of today's powerful computers, molecular modeling simulations have been advanced to such a level to predict physical properties of polymeric systems. In particular, molecular mechanics in combination with molecular dynamics (MD) method have been applied in the past decade in simulation studies of polymer dynamics in melts and solutions (Maranas et al., 1998). These techniques have been found effective methods to conduct studies of the structure and dynamics on the molecular-level, founded on reliable atomistic force fields.

However, the effect of high pressure on physical properties of polymer solutions based on a molecular perspective has not yet been accurately characterized. In relation to the characterization of pressure effects on thermophysical properties, a molecular perspective proves to be of great value in bringing some light on the changes in intra- and intermolecular interactions with pressure. In this regard, establishing a molecular-level characterization of density–pressure–composition relations in compressible polymer solutions is essential to thermodynamic processes and transport phenomena. To this end, we have revealed that the simulations performed in the NPT (constant mole number, pressure, and temperature) ensemble have the potential for accomplishing this objective. In previous work (Shahamat and Rey, 2012) we focused on developing a MD calculation platform under the isobaric–isothermal (NPT) ensemble to compute the effect of pressure on densities, structure (i.e. polymer radius of gyration and pair distribution functions), and cohesive energies of PE and hexane over a wide range of pressures from 100 up to 3000 bar by quantifying specific contributions of bonded/non-bonded interactions to gain a fundamental understanding of phase behavior in polymer solutions at high pressures. Furthermore, on the basis of the NPT–MD ensemble predictions of internal pressures were performed at elevated pressures and the knowledge of pressure dependence of solubility parameters and molar volumes was further utilized to build a molecular thermodynamic characterization of compressible PE solutions. In this regard, the Flory–Huggins binary interaction parameter, volume change upon mixing, and the chemical potential factor as functions of pressure were computed to predict miscibility and phase stability and to shed light on the pressure-induced phase separation mechanism in binary solutions of PE in hexane (Shahamat and Rey, 2013a).

The present work aims to contribute to the atomistic-level understanding of the pressure effects on binary solution density and structural properties of PE in hexane solutions at conditions of industrial interest, which have relevance to applied and fundamental polymer chemical physics based on MD simulations in the NPT ensemble. As established in previous work, (Ghiass and Rey, 2008) spinodals and binodals must be calculated by solving chemical and mechanical coupled balances, where the coupling involve compositional derivatives of pressure in addition to the usual compressibility. Furthermore, the kinetics of compressible phase separation, denoted acousto-spinodal decomposition, (Rasouli and Rey, 2011) integrates total mass, a component mass and momentum through compositional derivatives of pressure. Moreover, the binary solution densities are calculated using the MSL EOS model (as detailed below) to verify the accuracy of the proposed molecular modeling methodology.

Since in most cases non-bonded interactions dominate MD computations for large systems such as mixtures of polymer–solvent and polymer blends, it is of utmost importance to reduce the calculation time of the non-bonded forces while maintaining